

**JAPANESE**

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE  
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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**DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of an epoxy compound.

[0002]

[Description of the Prior Art]An epoxy compound is a compound important as various chemicals including resin, synthetic intermediate of those, etc.

Although the method of oxidizing using organicity-ized oxides, such as peroxy acids, such as m-chloroperbenzoic acid and peracetic acid, and tert-butylhydroperoxide, as the manufacturing method is known, olefins, for example, It was comparatively expensive and the peroxy acid and organic peroxide which require cautions for handling were used, and since post-processing after a reaction was also troublesome, development of the manufacturing method which uses neither a peroxy acid nor organic peroxide was desired.

[0003]On the other hand, hydrogen peroxide is cheap, handling is easy, moreover, after the reaction, it is clean and attention is attracted as an outstanding oxidizer used as harmless water in recent years. Hydrogen peroxide is made to react to olefins and the method of manufacturing an epoxy compound is reported variously.

For example, although the method (JP,8-27136,A) of making olefins and hydrogen peroxide react and manufacturing an epoxy compound under existence of alpha-aminomethylphosphonic acid, phase transfer catalysis, and tungstic acid, etc. are known, It was expensive and hygroscopicity was not

necessarily able to say it as the method which may be satisfied enough from an industrial viewpoint in that it is high and alpha-aminomethylphosphonic acid which requires cautions for handling must be used.

[0004]

[Problem(s) to be Solved by the Invention] This invention persons use a cheaply available agent under such circumstances, The tungsten oxide to which acquisition makes a tungsten compound and hydrogen peroxide, such as an easy tungsten metal and tungsten sulfide, come to react when how to manufacture an epoxy compound is examined wholeheartedly, Under existence of boric acid and phase transfer catalysis, by making olefins and hydrogen peroxide react, it found out that an epoxy compound was obtained and resulted at this invention.

[0005]

[Means for Solving the Problem] That is, this invention provides a manufacturing method of an epoxy compound making olefins and hydrogen peroxide react under existence of a tungsten oxide, boric acid, and phase transfer catalysis to which make a tungsten compound and hydrogen peroxide come to react.

[0006]

[Embodiment of the Invention] The olefins used for a raw material should just be the compounds which have one or more olefin nature carbon-carbon double bonds in intramolecular, and two carbon atoms which form this double bond, It may be replaced by substituents, such as everything but a hydrogen atom, for example, an alkyl group, an aryl group, an aralkyl group, a silyl group, a halogen atom, etc.

[0007] As an alkyl group, for example A methyl group, an ethyl group, n-propyl group, An isopropyl group, n-butyl group, an isobutyl group, a sec-butyl group, Straight chain shape, such as a tert-butyl group, n-pentyl group, n-hexyl group, n-octyl group, an isooctyl group, n-nonyl group, n-decyl group, a cyclopentyl group, and a cyclohexyl group, the shape of a branched chain, or an annular alkyl group is mentioned. This alkyl group may have a substituent and alkoxy groups, such as a methoxy group, an ethoxy basis, n-propoxy group, an isopropoxy group, and n-butoxy group, the silyl group mentioned later, the halogen atom mentioned later, etc. are mentioned as a substituent, for example.

[0008] As an aryl group, for example These phenyl groups, such as a phenyl group and a naphthyl group, To the aromatic ring which constitutes a naphthyl group etc., for example An alkyl group, an alkoxy group, . Substituents, such as acyl groups, such as a silyl group, a halogen atom, for example, an acetyl group, and a propionyl group, replaced. For example, 2-fluorophenyl group, 3-fluorophenyl group, 4-fluorophenyl group, 2-chlorophenyl group, a 3-chlorophenyl group, 4-chlorophenyl group, 2-bromo phenyl group, 2-methylphenyl group, 4-methylphenyl group, 4-methoxyphenyl group, 4-acetyl phenyl group, etc. are mentioned.

[0009] What comprises an above mentioned alkyl group and an above mentioned aryl group as an aralkyl group is mentioned, for example, benzyl, a phenylethyl group, 4-fluorobenzyl, 4-methoxybenzyl group, 2-chlorobenzyl, etc. are mentioned.

[0010] As a silyl group, trialkylsilyl groups, such as a trimethylsilyl group, a triethyl silyl group, a dimethylphenyl silyl group, and a methylphenyl silyl group, etc. are mentioned, for example, and a fluorine atom, a chlorine atom, a bromine atom, etc. are mentioned as a halogen atom, for example.

[0011] The substituent of the carbon atom which constitutes an olefin nature carbon-carbon double bond may become together, may form a part of ring structure, and it as a ring structure. For example, a cyclobutane ring, a cyclopentane ring, a cyclohexane ring, a cycloheptane ring, a cyclooctane ring, a

cyclo nonane ring, a cyclodecanering, a cyclododecanering, etc. are mentioned. Of course, this ring structure may be replaced by said alkyl group, said alkoxy group, said silyl group, said halogen atom, etc.

[0012]As these olefins, for example Ethylene, propylene, 1-butene, 1-pentene, 4,4-dimethyl- 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecen, 1-tridecenoic, 1-tetra decene, 1-pentadecene, 1-hexa decene, 1-octadecene, a 3,3-dimethyl- 1-butene, vinyl cyclopentane, 1 substitution olefins, such as vinylcyclohexane, allylcyclohexane, styrene, 4-(tert-butyl) styrene, allylbenzene, 4-methoxy styrene, a safrole, eugenol, and 3,4-dimethoxy- 1-allylbenzene, [0013]For example, 2-butene, isobutylene, a 2-methyl-1-butene, 2-pentene, 2-hexene, a 2-methyl-1-hexene, 3-hexene, 2-heptene, A 2-methyl-1-heptene, 3-heptene, 2-octene, 3-octene, 4-octene, 2-nonene, 2-methyl-2-nonene, 3-nonene, 4-nonene, 5-decene, 2-methyl-1-undecene, cyclopentene, Disubstituted olefin, such as a cyclohexene, 4-methylcyclohexene, cyclohepten, cyclooctane, cyclodecene, cyclo dodecen, methylenecyclohexane, beta-methylstyrene, a stilbene, isosafrole, isoeugenol, beta-pinene, and norbornene, [0014]For example, a 2-methyl-2-butene, a 2-methyl-2-pentene, a 2-methyl-2-hexene, 2,5-dimethyl- 2,4-hexadiene, a 2-methyl-2-heptene, 1-methylcyclopentene, 1-methylcyclohexene, 1-(tert-butyl) cyclohexene, 4 substitution olefins, such as 3 substitution olefins, for example, a 2,3-dimethyl- 2-butene, such as 1-isopropylcyclohexene, 2-Caren, 3-Caren, and an alpha pinene, and a 2,3,4-trimethyl 2-pentene, etc. are mentioned.

[0015]Although geometric isomer and an optical isomer exist in some of these olefins, independent geometric isomer and optical isomer may be used for this invention, and the mixture of geometric isomer and the mixture of an optical isomer may be used for it.

[0016]as a tungsten compound -- the [ a tungsten metal, tungsten, and ] -- the tungsten compound which consists of an IIIB group element. the [ tungsten and ] -- the [ the tungsten compound and tungsten which consist of an IVB group element, and ] -- the [ the tungsten compound and tungsten which consist of a VB group element, and ] -- the tungsten compound etc. which consist of a VIB group element are independent, or a mixture is mentioned.

[0017]the [ tungsten and ] -- as an IIIB group element compound, for example, tungsten boride etc. -- the [ tungsten and ] -- as a tungsten compound which consists of an IVB group element compound, for example, tungsten carbide etc. -- the [ tungsten and ] -- as a tungsten compound which consists of a VB group element, for example, Lynn-ized tungsten and tungsten nitride etc. -- the [ tungsten and ] -- as a tungsten compound which consists of a VIB group element, tungstic oxide, tungsten sulfide, tungstic acid, etc. are mentioned, for example.

[0018]Also in this tungsten compound, a tungsten metal, tungsten boride, tungsten carbide, and tungsten sulfide are preferred. It is preferred to use a tungsten compound with fine particle diameter at the point of making preparation of a tungsten oxide easier.

[0019]A tungsten oxide is prepared by making this tungsten compound and hydrogen peroxide react. As hydrogen peroxide, although usually used as solution, an organic solvent solution may be used. It is preferred to use a hydrogen-peroxide-solution solution in that handling is easier. Although the hydrogen peroxide concentration in particular in a hydrogen-peroxide-solution solution or an organic solvent solution is not restricted, when volume efficiency, a safety aspect, etc. are taken into consideration, it is 1 to 60 % of the weight practical. What is necessary is just to usually use a hydrogen-peroxide-solution solution, remaining as it is or after dilution, concentration, etc. perform concentration adjustment if needed, and a commercial thing the organic solvent solution of hydrogen peroxide. For example, it can prepare by carrying out extracting processing of the hydrogen-peroxide-solution solution, or carrying out distillation treatment under existence of an organic solvent with an

organic solvent, or other means.

[0020]The amount of the hydrogen peroxide used at the time of preparing a tungsten oxide is usually more than 5 mol twice preferably more than 3-mol double to a tungsten compound, and the maximum in particular does not exist.

[0021]The reaction of a tungsten compound and hydrogen peroxide is usually carried out in solution. Of course, for example, diethylether, methyl tert-butyl ether, Ester solvent, such as ether system solvents, for example, ethyl acetate etc., such as a tetrahydrofuran, For example, it may carry out in organic solvents, such as nitrile system solvents, such as tertiary-alcohol system solvents, for example, acetonitrile, such as tert-butanol, and propionitrile, or the mixed solvent of this organic solvent and water.

[0022]The preparation temperature at the time of preparation of a tungsten oxide is usually -10-100

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[0023]Although all or some of metallic compounds can dissolve and the homogeneous solution or suspension containing a metallic oxide can be prepared by making a tungsten compound and hydrogen peroxide react underwater or in an organic solvent, This metallic oxide may be picked out from a prepared solution, for example by condensation processing etc., and may be used as a catalyst, and this prepared solution may be used as a catalyst as it is.

[0024]In order to raise the contacting efficiency of a tungsten compound and hydrogen peroxide, it is preferred to react stirring so that a tungsten compound may distribute enough in a tungsten oxide prepared solution. It is preferred to use tungsten compounds with small particle diameter, such as a powdered tungsten compound, for example in that raise the contacting efficiency of a tungsten compound and hydrogen peroxide, and control at the time of metallic-oxide preparation is made easier.

[0025]As boric acid, perboric acid alkali metal salt, such as boric acid alkali metal salt, for example, sodium perborate etc., such as boric acid and ammonium pentaborate, for example, the sodium borate etc., etc. are mentioned, for example. A hydrate may be used for that in which a hydrate exists among these boric acid. For example, what boric acid and alkali metal hydroxide were made to react, and was prepared may be used for boric acid alkali metal salt.

[0026]the amount of the boric acid used receives a tungsten oxide -- usually -- usually -- 0.1-4-mol twice -- it is 0.3-2-mol twice preferably.

[0027]These boric acid may be used in the case of the beforehand above-mentioned tungsten oxide preparation.

[0028]As phase transfer catalysis, quarternary ammonium salt, quaternary phosphonium salt, and macrocyclic polyether are mentioned, for example, and quarternary ammonium salt is preferred.

[0029]As quarternary ammonium salt, for example Trioctyl methylammonium chloride, Trioctyl ethylammonium chloride, dilauryl dimethylammonium chloride, Lauryl trimethylammonium chloride, stearyl trimethylammonium chloride, Lauryldimethyl benzylammonium chloride, TORIKA prill methylammonium chloride, Tridecyl methylammonium chloride, trihexyl methylammonium chloride, Tridodecyl methylammonium chloride, tetrabutyl ammonium chloride, Benzyl trimethylammonium chloride, benzyl triethyl ammonium chloride, N-lauryl pyridiniumchloride, N-cetyl pyridinium chloride, Quaternary ammonium chloride, such as N-lauryl pico RINIUMU chloride. The quaternary ammonium bromide which the chloride ion which constitutes said quaternary ammonium chloride replaced with the bromine ion. The chloride ion which constitutes the quaternary ammonium iodide which the chloride ion which constitutes said quaternary ammonium chloride replaced with iodine ion,

and said quaternary ammonium chloride, The quaternary ammonium sulfite salt which replaced sulfite ion, and the chloride ion which constitutes said quaternary ammonium chloride, The quaternary ammonium hydrogensulfate etc. which the chloride ion which constitutes the quaternary ammonium sulfate replaced with sulfate ion and said quaternary ammonium chloride replaced with the sulfuric acid hydrogen ion are mentioned.

[0030]Tetrabutylphosphonium bromide etc. are mentioned as quaternary phosphonium salt, and the 12-crown 4, the 18-crown 6, and benzo-18-crown 6 grade are mentioned as macrocyclic polyether, for example.

[0031]The amount of [ in the case used of using this phase transfer catalysis ] is usually more than 0.0005 mol twice to olefins, and although the maximum in particular does not exist, when an economical field is taken into consideration, it is less than 1 mol twice to olefins practical. This phase transfer catalysis may be used in the case of the beforehand above-mentioned tungsten oxide preparation.

[0032]As hydrogen peroxide made to react to olefins, hydrogen peroxide solution is usually used. Of course, hydrogen peroxide/organic solvent solution may be used. Although the hydrogen peroxide concentration in particular in hydrogen peroxide solution, or hydrogen peroxide/organic solvent solution is not restricted, when volume efficiency, a safety aspect, etc. are taken into consideration, it is 1 to 60 % of the weight practical.

[0033]To olefins, it is more than 1 mol twice preferably, and although the maximum in particular does not exist, more than 0.8 mol twice and since it is easy to become disadvantageous economically even if too not much large, the amount of the hydrogen peroxide used is usually less than 3 mol twice preferably below 5-mol double to olefins practical.

[0034]the amount of the metal oxide catalyst used receives olefins as metal -- usually -- 0.001-0.95-mol twice -- it is 0.005-0.1-mol twice preferably.

[0035]A non-solvent may perform the reaction with olefins and hydrogen peroxide, and it may carry out in an aqueous solvent or an organic solvent. As an organic solvent, for example Aromatic hydrocarbon system solvents, such as toluene and xylene, For example, aliphatic hydrocarbon system solvents, for example, diethylether, such as hexane and heptane, Nitrile system solvents, such as tertiary-alcohol system solvents, for example, acetonitrile, such as ester solvent, for example, tert-butanol etc., such as ether system solvents, for example, ethyl acetate etc., such as methyl tert-butyl ether, a tetrahydrofuran, and a jig lime, and propionitrile, etc. are mentioned. The amount in particular of an aqueous solvent or the organic solvent used is not restricted.

[0036]This reaction is usually performed by contacting and mixing a tungsten oxide, boric acid, phase transfer catalysis, olefins, and hydrogen peroxide, and the mixed sequence foreword in particular is not restricted. For example it may contact, a tungsten compound, hydrogen peroxide, boric acid, phase transfer catalysis, and olefins may be mixed, and the reaction of preparation operation of a tungsten oxide, and olefins and hydrogen peroxide may be performed simultaneously.

[0037]Although reaction temperature is usually 0-130 °C and is usually carried out under ordinary pressure conditions, it may be carried out under decompression or a pressurizing condition.

[0038]Although an epoxy compound generates with advance of a reaction, advance of this reaction can be checked, for example by the usual tools of analysis, such as a gas chromatography, high speed liquid chromatography, thin layer chromatography, NMR, and IR.

[0039]After ending reaction, after reducing agents, such as sodium sulfite, decompose the hydrogen peroxide which remains as it is or remains if needed for reaction mixture, for example, the target epoxy compound can be taken out by carrying out condensation processing, crystallization processing,

etc. An epoxy compound can also be taken out by carrying out condensation processing of the organic layer obtained by adding and carrying out extracting processing of the organic solvent insoluble to water and/or water to reaction mixture if needed. The taken-out epoxy compound may be further refined, for example with the usual refining methods, such as distillation, column chromatography, and recrystallization.

[0040] As an epoxy compound obtained in this way, for example Ethylene oxide, Propylene oxide, 1,2-epoxy butane, 1,2-epoxy pentane, 4,4-dimethyl- 1,2-epoxy pentane, 1,2-epoxy hexane, 1,2-epoxy heptane, 1,2-epoxy octane, 1,2-epoxy nonane, A 1,2-epoxy decane, a 1,2-epoxy undecane, a 1,2-epoxy dodecane, A 1,2-epoxy tridecane, 1,2-epoxy tetradecane, 1,2-epoxy pentadecane, 1,2-epoxy hexadecane, 1,2-epoxy octadecane, 3,3-dimethyl- 1,2-epoxy butane, Cyclopentylethylene oxide, cyclohexylethylene oxide, 3-cyclohexyl-1,2-epoxypropane, styrene oxide, 4-(tert-butyl) styrene oxide, 3-phenyl-1,2-epoxypropane, 4-methoxy styrene oxide, saffroleoxide, 3-(4-hydroxy-3-methoxyphenyl)-1,2-epoxy propane, 3-(3,4-dimethoxyphenyl)-1,2-epoxy propane, 2,3-epoxy butane, 2-methyl-1,2-epoxypropane, 2-methyl-1,2-epoxy butane, 2,3-epoxy pentane, 2,3-epoxy hexane, 2-methyl-1,2-epoxy hexane, 3,4-epoxy hexane, 2,3-epoxy heptane, 3,4-epoxy heptane, 2,3-epoxy octane, 3,4-epoxy octane, 4,5-epoxy octane, 2,3-epoxy nonane, [0041] 2-methyl-1,2-epoxy nonane, 3,4-epoxy nonane, 4,5-epoxy nonane, A 5,6-epoxy decane, a 2-methyl-1,2-epoxy undecane, Cyclopenteneoxide, cyclohexane oxide, 4-methyl cyclohexane oxide, Cyclohepten oxide, cyclooctaneoxide, cyclodecene oxide, Cyclo dodecen oxide, beta-methylstyreneoxide, stilbeneoxide, Isosaffroleoxide, 1-(4-hydroxy-3-methoxyphenyl)-1,2-epoxy propane, beta-pineneoxide, norbornene oxide, 2-methyl-2,3-epoxy butane, 2-methyl-2,3-epoxy pentane, 2-methyl-2,3-epoxy hexane, 2,5-dimethyl- 2,3-epoxy hex-4-ene, 2-methyl-2,3-epoxy heptane, 1-methyl-1,2-epoxy cyclopentane, 1-methyl-1,2-epoxy cyclohexane, 1-(tert-butyl)-1,2-epoxy cyclohexane, 1-isopropyl-1,2-epoxy cyclohexane, 2-Karen oxide, 3-Karen oxide, alpha pinene oxide, 2,3-dimethyl- 2,3-epoxy butane, 2,3,4-trimethyl 2,3-epoxy pentane, etc. are mentioned.

[0042]

[Example] Hereafter, although an example explains this invention still in detail, this invention is not limited to this example.

[0043] The nitrogen purge of the 100mL SHURENKU pipe which attached the example 1 flowing-back condenser tube was carried out, at the room temperature, the tungsten metal 0.15g and the 30-% of the weight hydrogen peroxide solution 7.2g were prepared, it stirred with the internal temperature of 50 °C for 15 minutes, and the tungsten oxide prepared solution was obtained. Cool this prepared solution to a room temperature, and the sodium-borate solution which consists of the boric acid 0.025g, 0.064g of sodium hydroxide, and water 0.25mL is added, After stirring for 3 minutes, the solution which consists of 4.4 g of cyclooctane, 0.19g of trioctyl methylammonium hydrogensulfate, and toluene 8mL is prepared, and it stirred, held to this for 4 hours, and was made to react to it with the internal temperature of 90 °C. The obtained reaction mixture was cooled, liquid separation processing was carried out, and the organic layer containing cyclooctaneoxide was obtained. The yield of cyclooctaneoxide was 62% when the gas chromatography (internal standardization) analyzed this organic layer (cyclooctane standard).

[0044] In comparative example 1 Example 1, except not using the sodium-borate solution which consists of the boric acid 0.025g, 0.064g of sodium hydroxide, and water 0.25mL, it carried out like Example 1 and the organic layer containing cyclooctaneoxide was obtained. The yield of cyclooctaneoxide was 26% when the gas chromatography (internal standardization) analyzed this organic layer (cyclooctane standard).

[0045]The nitrogen purge of the 100mL SHURENKU pipe which attached the example 2 flowing-back condenser tube was carried out, at the room temperature, the tungsten metal 0.15g and the 30-% of the weight hydrogen peroxide solution 7.2g were prepared, it stirred with the internal temperature of 50 °C for 15 minutes, and the tungsten oxide prepared solution was obtained. Cool this prepared solution to a room temperature, and the sodium-borate solution which consists of the boric acid 0.025g, 0.064g of sodium hydroxide, and water 0.25mL is added, After stirring for 3 minutes, the solution which consists of 4.5 g of 1-octene, 0.19g of trioctyl methylammonium hydrogensulfate, and toluene 8mL is prepared, and it stirred, held to this for 4 hours, and was made to react to it with the internal temperature of 90 °C. The obtained reaction mixture was cooled, liquid separation processing was carried out, and the organic layer containing 1,2-epoxy octane was obtained. When the gas chromatography (internal standardization) analyzed this organic layer, the yield of 1,2-epoxy octane was 27% (1-octene standard).

[0046]In comparative example 2 Example 2, except not using the sodium-borate solution which consists of the boric acid 0.025g, 0.064g of sodium hydroxide, and water 0.25mL, it carried out like Example 2 and the organic layer containing 1,2-epoxy octane was obtained. When the gas chromatography (internal standardization) analyzed this organic layer, the yield of 1,2-epoxy octane was 1% (1-octene standard).

[0047]The nitrogen purge of the 100mL SHURENKU pipe which attached the example 3 flowing-back condenser tube was carried out, at the room temperature, the tungsten metal 0.15g and the 30-% of the weight hydrogen peroxide solution 7.2g were prepared, it stirred with the internal temperature of 50 °C for 15 minutes, and the tungsten oxide prepared solution was obtained. Cool this prepared solution to a room temperature, and the sodium-borate solution which consists of the boric acid 0.025g, 0.064g of sodium hydroxide, and water 0.25mL is added, After stirring for 3 minutes, the solution which consists of 3-Caren 5.5g, 0.19g of trioctyl methylammonium hydrogensulfate, and toluene 8mL is prepared, and it stirred, held to this for 4 hours, and was made to react to it with the internal temperature of 70 °C. The obtained reaction mixture was cooled, liquid separation processing was carried out, and the organic layer containing 3-Karen oxide was obtained. When the gas chromatography (internal standardization) analyzed this organic layer, the yield of 3-Karen oxide was 19% (3-Caren standard).

[0048]In comparative example 3 Example 3, except not using the sodium-borate solution which consists of the boric acid 0.025g, 0.064g of sodium hydroxide, and water 0.25mL, it carried out like Example 3 and the organic layer containing 3-Karen oxide was obtained. When the gas chromatography (internal standardization) analyzed this organic layer, the yield of 3-Karen oxide was 1% (3-Caren standard).

[0049]In example 4 Example 1, cyclooctanoxide is obtained by carrying out like Example 1 except replacing with a tungsten metal and using tungsten boride.

[0050]In example 5 Example 1, cyclooctanoxide is obtained by carrying out like Example 1 except replacing with a tungsten metal and using tungsten carbide.

[0051]In example 6 Example 1, cyclooctanoxide is obtained by carrying out like Example 1 except replacing with a tungsten metal and using tungsten sulfide.

[0052]

[Effect of the Invention]In this invention, acquisition uses the metal oxide catalyst which can be prepared easily from a tungsten compound, boric acid, hydrogen peroxide, and phase transfer catalyses, such as an easy tungsten metal.

Therefore, since an epoxy compound is obtained by a reaction with olefins and hydrogen peroxide, it

is industrially advantageous.

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